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MEMORANDUM

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SUBJECT: DETERMINATION OF MITC SOIL FLUX DENSITY AND EMISSION RATIO FROM A FIELD FOLLOWING A TARPED BED DRIP APPLICATION OF METAM SODIUM

Introduction:

With the phase out of methyl bromide, metam sodium has become the number one soil fumigant in California with 15 million pounds use annually. After application, metam sodium ($C_2H_4NaS_2$) breaks down into methyl isothiocyanate (CH_3NCS), also known as MITC, a highly toxic compound capable of killing a wide spectrum of soil-borne pests. Therefore, metam sodium is considered as one of best alternatives for methyl bromide. As metam sodium is applied in liquid form, the effectiveness of metam sodium as a soil fumigant largely depends on the uniformity of its distribution in treated fields.

The Department of Pesticide Regulation requested the Air Resources Board (ARB) conduct MITC air monitoring following a tarped drip application of metam sodium (June 28, 2000, Helliker to Lloyd Memorandum, and July 25, 2001, Sanders to Cook, Memorandum). This memorandum reports results of MITC flux estimation by the back calculation method (Johnson et al., 1999) using MITC air concentrations obtained during the ARB air monitoring study.

Material and Methods:

<u>Field Description, Chemigation, and Air Sampling:</u>

Air monitoring was conducted from May 7-12, 2002 in Ventura County, at a field treated with metam sodium through drip irrigation system (ARB 2004). The treated field consisted of two plots, one rectangle and one of irregular shape. The two plots were 9.15m (30ft) apart (Figure 1, attached). The field size was approximately 35,775m^2 (8.84 acres). Eighty-four rows of drip lines were evenly spaced through the field. Each row was 1.73m (68 inches) wide, however, the drip line length varied from 189.4m to 290.3m (7,452 inches to 11,420 inches).

Sectagon 42® (42.2% metam sodium by weight) was applied by tarped bed drip chemigation. The actual application rate over treated area was 60.6g/m^2 (541 lbs/treated-acre) and the effective broadcast rate of metam sodium was 26.8g/m^2 (239 lbs/acre). The molecular weights of metam sodium and MITC are 129.2g/mol and 73.1g/mol, respectively, and the conversion ratio from metam sodium to MITC is 1:1. Therefore, the equivalent MITC application rate was 15.2g/m^2.

Eight air samplers, one on each side and one at each corner, were positioned 11.6m to 20.7m (38ft to 65ft) from the field edge (Figure 1, attached). Sampling interval was approximately 12-hour duration, from sunset to sunrise or from sunrise to sunset, representing overnight and daytime concentrations respectively. The first sampling interval covered application and post-application hours (2.67 hours during the application and 9.33 hours immediately following the application). The average air concentration over each sampling interval was determined through laboratory analysis of air samples.

A weather station was located at the southwest corner of the field (Figure 1, attached). Weather elements, including air temperature and wind speed as well as wind direction, were averaged every 15 minutes, and stored into a data logger.

<u>Modeling Air Concentration With ISCST3 Dispersion Model:</u>

The U.S. Environmental Protection Agency (U.S. EPA) ISCST3 model is capable of modeling the spatial-temporal distribution of air concentration from various emission sources. The ISCST3 model requires as input the geometry of emission source, emission rate, meteorology conditions, and location of receptors. The process of preparing and running the ISCST3 model is described in detail in the User's Guide of ISCST3 model (U.S. EPA, 1995 and 2002), and in a Department of Pesticide Regulation publication (Johnson et al, 1999).

<u>Field Geometry and Receptor Location</u>:

Based on the field information provided by ARB, source geometry and receptor location were quantified with a user-defined coordinate system (Figure 1, attached). The origin point is located in the southwest corner of the field. Under this coordinate system, the locations of receptors are shown in Table 1.

Table 1. X and Y coordinate of air monitoring receptors

Receptor ID	Receptor Location	X(m)	Y(m)
1	NE	159.0	304.0
2	E	165.0	189.6
3	SE	158.0	86.6
4	S	72.5	34.0
5	SW	-14.0	-12.8
6	W	-19.8	147.0
7	NW	-14.0	304.0
8	N	72.5	310.0

The upper bed was a rectangle, an area easily defined by four corner points. The lower bed was an irregular shape, but could be approximated by a polygon (Figure 2, attached) (U.S. EPA, 2002). The polygon was defined by a series of vertex of corner points (Table 2).

Table 2. Vertex of the polygon that approximates the lower field bed

Point	X(m)	Y(m)
1	0	12
2	6	3
3	30	0
4	60	35
5	145	100
6	145	146
7	0	146
8	0	12

Meteorology and Stability Classification:

Weather data were processed to generate hourly average meteorological data in the format compliant to the ISCST3 model requirements (Johnson et al, 1999). To determine the stability class of each hour, sunrise time, sunset time, and solar elevation angle was calculated by running a computer program using latitude and Julian day as input variables (Johnson et al, 1999). A program (Appendix-I, attached) was developed to streamline stability class determination based on look-up tables for stability classification (Budney, 1977). The program uses wind speed, day/night, cloud type, sky cover, and solar elevation as input variables and outputs Pasquill stability class. Cloud type was assumed to be thin high clouds and sky coverage zero. The program also adjusts stability class, so that stability classes of two adjacent hours do not differ by more than one class. When adjusting stability class, results would differ slightly if the starting hours differ. The hourly meteorological data file used as ISCST3 input is attached at the end of this memo (Appendix-II, attached).

Running the ISCST3 mode:

Input variables described above were input into the ISCST3 model through a control file. In this study, we are interested in modeling the average air concentration over each sampling period. Therefore, there was a control file and a meteorological file corresponding to each air sampling period. When running the ISCST3 model, a nominal soil flux density (E_0) of 0.0001g/m^2-s was used for all five periods. An example of a control file is illustrated in Appendix-III.

Back Calculation of Soil Flux Density:

The soil flux density was determined through a back calculation procedure, in which measured air concentration was regressed to the simulated air concentration:

$$C_m = a + bC_s \tag{1}$$

where C_m and C_s represent measured and simulated air concentration respectively, 'a' and 'b' were intercept and slope of the regression line. The 95% confidence intervals for the slope and intercept were calculated (Agresti and Finlay, 1986) to examine if a regression was statistically significant.

In the Gaussian model simulated air concentrations are directly proportional to the source flux density. The back calculation procedure uses the slope of the regression line to adjust the nominal soil flux density in order to produce simulated air concentrations of the same magnitude observed in the measured air concentrations:

$$E = bE_0 \tag{2}$$

where E_0 (g/m^2-s) is the nominal soil flux density used in ISCST3 modeling, 'b' is the slope of regression line, and E (g/m^2-s) is the estimated soil flux density. The MITC emission ratio (R) is calculated as:

$$R = \frac{E \times 12 \times 3600}{A} \tag{3}$$

where A is the effective broadcast application rate of MITC (15.2g/m^2), and E (g/m^2-s) is the estimated soil emission flux density. Constants 12 and 3600 are time conversion coefficients (assuming 12 hours for each period).

Adjustment with Spike Recovery Rate:

The recovery rate of the lab spikes, trip spikes, and field spikes ranged from 55% to 80% in this study. Therefore, the soil flux density and emission ratio should be adjusted by the recovery rate of spikes. The lower limits of the soil flux density and emission ratio were E and R respectively, and the upper limits were estimated as E/0.55 and R/0.55 respectively.

Results:

Simulated Air Concentrations:

Simulated air concentrations generally agreed with measured values (Table 3). When MITC was not detected (below the Method Detection Limit), simulated air concentrations were either zero or a small value, with just a few exceptions.

Table 3. Measured and simulated air concentrations for each sampling period and location around the field

Period	Receptor Location	On Date	Time	Off Date	Time	Run Time (min)	MITC Air Concentration (:g/m^3) Measured	Simulated
1	W	05/09/02	703	05/09/02	1810	667	MDL	0
1	S	05/09/02	708	05/09/02	1830	682	6	24
1	E	05/09/02	712	05/09/02	1900	708	25	509
1	N	05/09/02	718	05/09/02	1935	737	32	541
1	NW	05/09/02	700	05/09/02	1800	660	MDL	0
1	NE	05/09/02	715	05/09/02	1923	728	32	794
1	SE	05/09/02	710	05/09/02	1850	700	6	9
1	SW	05/09/02	705	05/09/02	1820	675	MDL	0
2	NW	05/09/02	1807	05/10/02	548	701	6	433
2	W	05/09/02	1818	05/10/02	557	699	35	2559
2	SW	05/09/02	1825	05/10/02	610	705	15	1418
2	S	05/09/02	1848	05/10/02	615	687	25	500
2	SE	05/09/02	1857	05/10/02	623	686	10	391
2	E	05/09/02	1917	05/10/02	630	673	11	424
2	NE	05/09/02	1930	05/10/02	645	675	10	517
2	N	05/09/02	1943	05/10/02	653	670	9	597
3	NW	05/10/02	553	05/10/02	1715	682	MDL	0
3	W	05/10/02	600	05/10/02	1725	685	1	132
3	SW	05/10/02	613	05/10/02	1735	682	MDL	142
3	S	05/10/02	620	05/10/02	1745	685	1	33
3	SE	05/10/02	625	05/10/02	1757	692	1	0
3	E	05/10/02	635	05/10/02	1808	693	9	349
3	NE	05/10/02	648	05/10/02	1830	702	12	647
3	N	05/10/02	655	05/10/02	1840	705	15	547
4	NW	05/10/02	1720	05/11/02	544	744	1	0
4	W	05/10/02	1730	05/11/02	552	742	13	2155
4	SW	05/10/02	1740	05/11/02	603	743	12	1767
4	S	05/10/02	1752	05/11/02	610	738	11	607
4	SE	05/10/02	1802	05/11/02	622	740	1	0
4	E	05/10/02	1815	05/11/02	632	737	2	146
4	NE	05/10/02	1835	05/11/02	650	735	3	273
4	N	05/10/02	1848	05/11/02	659	731	3	318
5	W	05/11/02	558	05/11/02	1702	664	MDL	277
5	SW	05/11/02	607	05/11/02	1727	680	MDL	41
5	S	05/11/02	618	05/11/02	1737	679	1	31
5	SE	05/11/02	626	05/11/02	1750	684	1	12
5	E	05/11/02	638	05/11/02	1806	688	6	486
5	NE	05/11/02	655	05/11/02	1834	699	7	577
5	N	05/11/02	705	05/11/02	1841	696	6	300

Method Detection Limit, 0.1 :g/sample

Regression:

Measured air concentrations (Y) were regressed on simulated air concentrations (X) for each period separately (Figure 3, attached). For all periods, the intercept of the regression was not significantly different from zero and slope was significantly different from zero (Table 4). All regressions were significant at 95% level.

Table 4. The 95% confidence interval for regression intercept (a) and slope (b), and R^2

Period	a			b			R^2		
	Estimate	CI1	CI2	Estimate	CI1	CI2	Estimate	CI1	CI2
1	2.530	-1.822	6.883	0.043027	0.031706	0.054347	0.94	0.68	0.99
2	6.463	-2.424	15.351	0.010133	0.002165	0.018101	0.62	0.03	0.92
3	-0.389	-3.062	2.283	0.022767	0.014701	0.030833	0.89	0.50	0.98
4	2.005	-0.768	4.778	0.005689	0.002972	0.008407	0.81	0.29	0.97
5	0.117	-2.016	2.251	0.011638	0.004613	0.018662	0.73	0.15	0.95

Soil Flux Density and Emission Ratio:

The peak soil flux density ranged from 4.30 to 7.82:g/m^2-s, occurred in the first sampling period which consisted of hours during the application and post application hours before the sunset. Soil flux density showed a general decline over time, but diurnal patterns were evident. Emission during the daytime was stronger than during the nighttime. Daytime soil flux density decreased by about 50% each day and the soil flux density for the second night period was also about the 56% of the first night period. About 1.22% to 2.22% MITC was lost in the first 12 hours and 2.65% to 4.82% in the first 60 hours, after application. The emission rate in the second day was about 53.5% of the first day.

Table 5. Soil flux density and emission ratio in sampling periods following chemigation

Period	Day/Night	b	Soil Flux Density (:g /m^2-s)		Emission Ratio[a]		Cumulative Emission Ratio	
			Lower Limit	Upper Limit	Lower Limit	Upper Limit	Lower Limit	Upper Limit
1	Day	0.0430	4.30	7.82	0.0122	0.0222	0.0122	0.0222
2	Night	0.0101	1.01	1.84	0.0029	0.0052	0.0151	0.0275
3	Day	0.0228	2.28	4.14	0.0065	0.0118	0.0216	0.0392
4	Night	0.0057	0.57	1.03	0.0016	0.0029	0.0232	0.0422
5	Day	0.0116	1.16	2.12	0.0033	0.0060	0.0265	0.0482

[a] Period duration was 12 hours

Conclusions:

In all five monitoring periods simulated and measured MITC air concentrations were in reasonable agreement. The soil flux density illustrated an apparent diurnal pattern, with daytime stronger than nighttime. The peak soil flux density was from 4.30 to 7.82:g/m^2-s, occurred in the first 12 hours of chemigation. Soil flux density decreased at a rate of 50% daily after chemigation. The cumulative MITC emission ratio from soil in the first 60 hours was about from 2.65% to 4.82%, of which 57% occurred in the first 24 hours.

Acknowledgements:

The author appreciates the help from Pam Wofford, who provided data and documents for this analysis, and reviewed the memo. Dr. Terrel Barry provided many valuable comments that greatly improved the analysis.

Attachments

cc: Pam Wofford, DPR Associate Environmental Research Scientist (w/ attachments)
Terrel Barry, DPR Senior Environmental Research Scientist (w/ attachments)

bcc: Li Surname File (w/ attachments)

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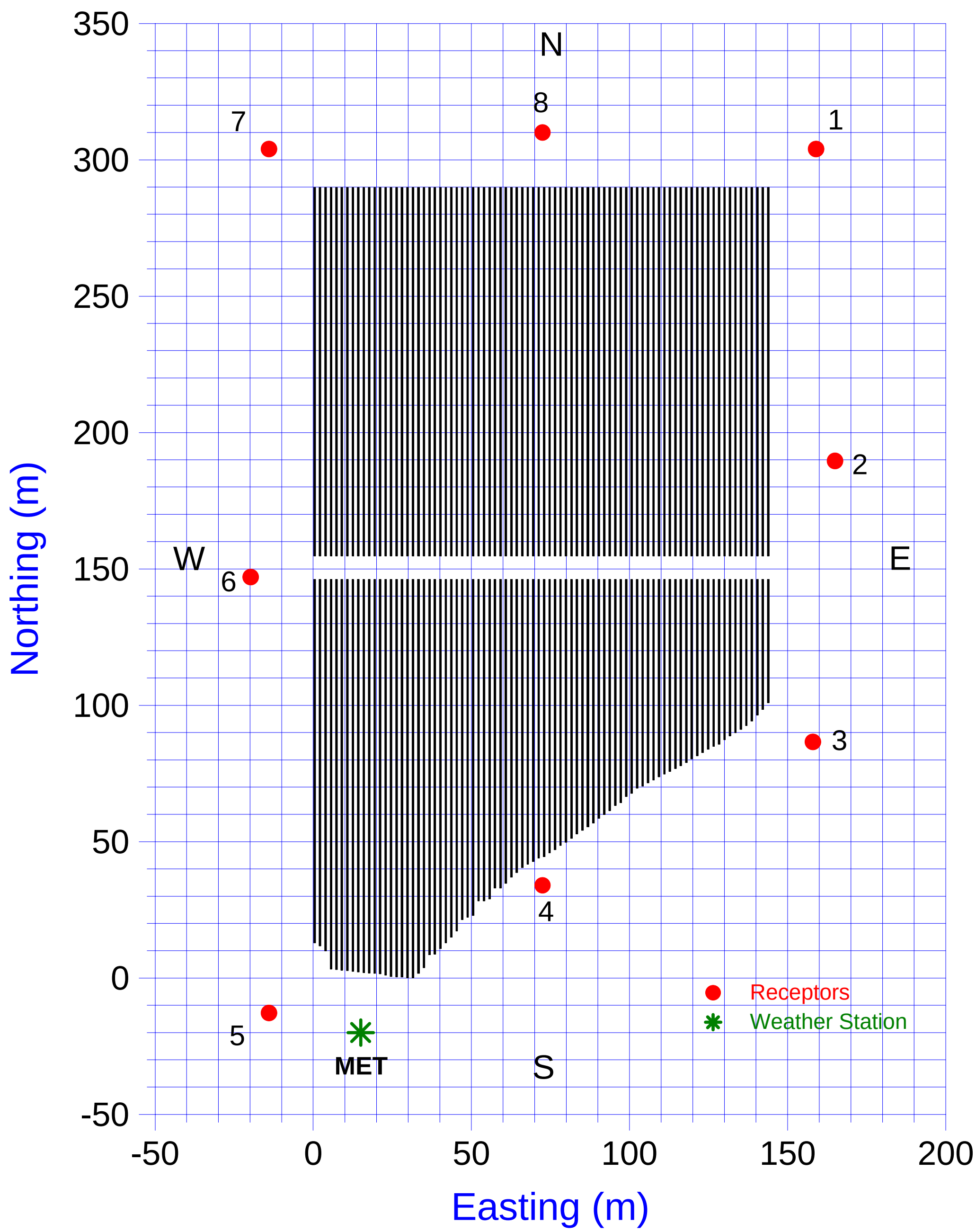

Figure 1 Layout of drip lines, receptor locations, and location of weather station

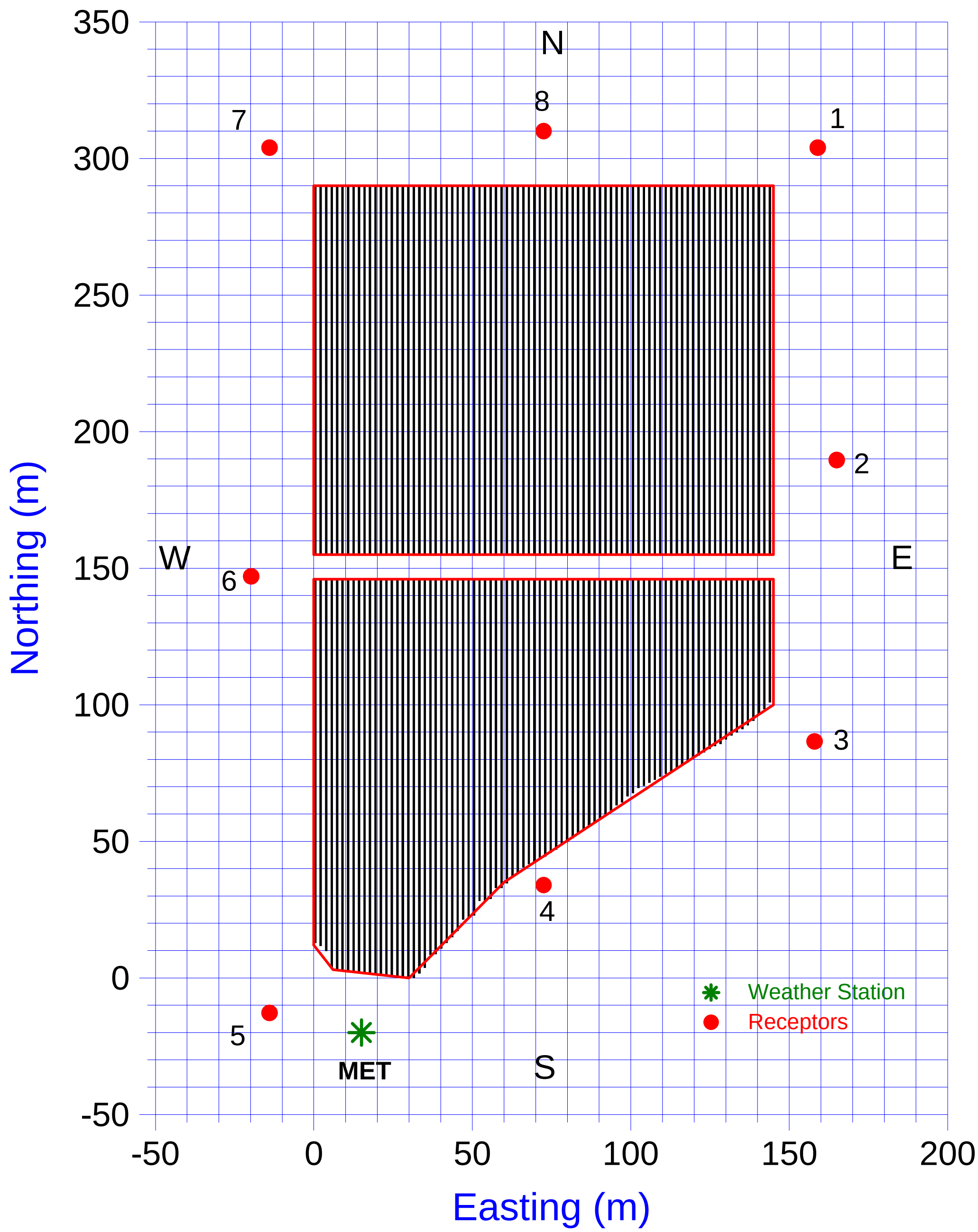

Figure 2 Approximating the chemigation fields with one rectangle and one polygon

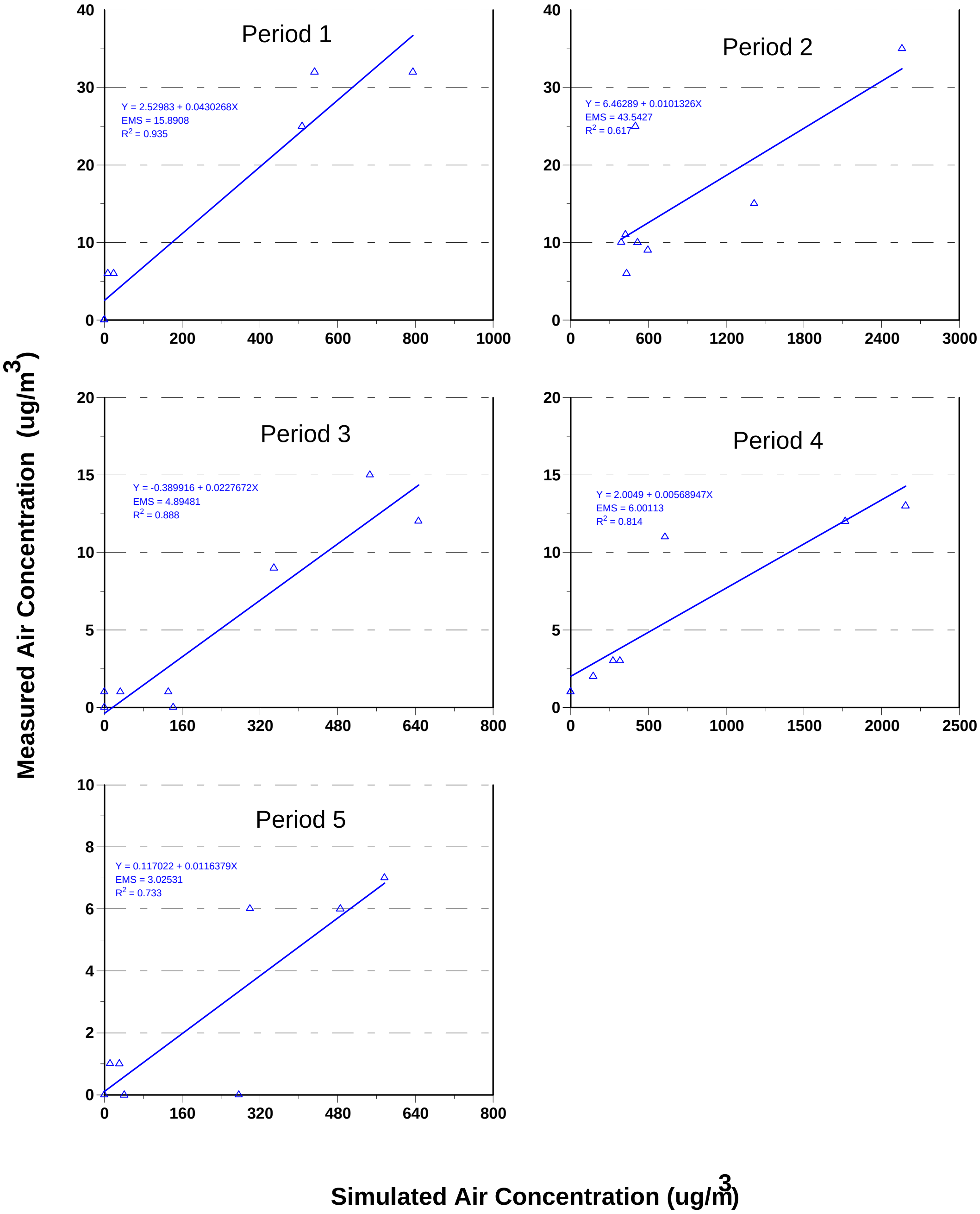

Figure 3 Regressions between measured and simulated air concentrations for various periods